

Lattice Dynamics of $\text{LaFeAsO}_{1-x}\text{F}_x$ and PrFeAsO_{1-y} via Inelastic X-Ray Scattering and First-Principles Calculation

Tatsuo FUKUDA^{1,2*}, Alfred Q.R. BARON^{1,3†}, Shin-ichi SHAMOTO⁴, Motoyuki ISHIKADO⁴, Hiroki NAKAMURA⁵, Masahiko MACHIDA⁵, Hiroshi UCHIYAMA^{1,3}, Satoshi TSUTSUI³, Akira IYO⁶, Hijiri KITO⁶, Jun'ichiro MIZUKI², Masatoshi ARAI⁷, Hiroshi EISAKI⁶, Hideo HOSONO⁸

¹Materials Dynamics Laboratory, SPring-8/RIKEN, Sayo, Hyogo 679-5148

²Synchrotron Radiation Research Unit, SPring-8/JAEA, Sayo, Hyogo 679-5148

³Research and Utilization Division, SPring-8/JASRI, Sayo, Hyogo 679-5198

⁴Neutron Materials Research Center, JAEA, Naka, Ibaraki 319-1195

⁵CREST, JST and the Center for Computational Science and e-Systems, JAEA, Taito, Tokyo 110-1195

⁶Nanoelectronics Research Institute (NeRI), AIST, Tsukuba, Ibaraki 305-8568

⁷J-PARC Center, JAEA, Naka, Ibaraki 319-1195

⁸ERATO-SORST, JST and Frontier Research Center, Tokyo Institute of Technology, Yokohama, 226-8503

The lattice dynamics of $\text{LaFeAsO}_{1-x}\text{F}_x$ ($x=0, 0.1$) and PrFeAsO_{1-y} ($y \sim 0.1$) are investigated using inelastic x-ray scattering and *ab-initio* calculation. Measurements of powder samples provide an approximation to the phonon DOS, while dispersion is measured from a single crystal of PrFeAsO_{1-y} . A model that agrees reasonably well with all of the data at room temperature is built from results of *ab-initio* calculations by reducing the strength of the Fe-As bond by 30%.

KEYWORDS: phonon density of states, dispersion relation, softening, iron-based superconductor, inelastic x-ray scattering, first-principles calculation

The recent discovery of high-temperature superconductivity in iron-arsenic materials,¹⁻³ with T_c exceeding 50K in some compounds,^{4,5} has led to an outpouring of work reminiscent of that following the discovery of the high T_c of MgB_2 .⁶ In the latter case, the synergy of experiment and calculation quickly demonstrated that MgB_2 was an exotic phonon-mediated superconductor. Despite the complexity of the new Fe-As compounds as compared to MgB_2 , calculations of phonon properties have appeared quickly,^{7,8} and seem to support the assertion that these materials are not phonon mediated.^{8,9} However, these calculations require experimental verification. Here we show that measurements of the phonon density of states (DOS) in several samples, and phonon dispersion in a single crystal of PrFeAsO_{1-y} do not agree with LDA-based calculations, including those referenced above. However, the calculations can be brought into much closer agreement with the data by softening the Fe-As bond. This highlights the failure of the calculations to predict the properties of the most important bond in this system, and suggests that the results of those calculations, especially regarding phonon behavior, should be carefully considered.

It is early to survey the properties of the FeAs superconductors, as information is very quickly evolving. However, the available phonon calculations based on pseudopotential methods are essentially consistent with each other,^{7,8} and with our calculations here, and do not indicate strong electron-phonon coupling.⁸ Calculations using a rigid ion model also suggest small electron-phonon coupling.⁹ The phonon DOS of a material provides a first,

global, look at phonon behavior. In this case, it allows us to develop a model of the dynamics based on the softening of just the Fe-As bond, which agrees reasonably with the data. The agreement is confirmed by comparison with spectra measured from a single crystal of PrFeAsO_{1-y} .

All measurements were made using ~ 1.5 meV resolution at 21.75 keV at BL35XU¹⁰ of SPring-8. The LaFeAsO and $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$ powder samples were synthesized as discussed in ref. 1 and the PrFeAsO_{1-y} was prepared using a high-pressure growth as in ref. 5. X-ray diffraction showed the polycrystalline samples to be predominantly single phase, and a careful four-circle investigation of the single crystal, $150 \times 100 \times 20 \mu\text{m}^3$, showed it to be a single grain, with a mosaic spread of about 1° . T_c of the samples were found to be 27K for the powder of $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$ and 48K for PrFeAsO_{1-y} , consistent with refs. 1,5 and 36K for the single crystal. About 50 mg of each powder was gently pressed into a tube with a diameter of 3 mm to form a flat surface for reflection-based inelastic x-ray scattering measurements (they were confirmed to be un-oriented after pressing) while the single crystal was mounted on a thin glass capillary and measured in a Laue geometry.

Calculations of the phonon spectra of LaFeAsO were carried out using the relaxed tetragonal $P4/nmm$ structure from VASP¹¹ calculated using a PAW method¹² and the GGA. Phonons were then calculated via the PHONON package using a direct method,¹³ in contrast to the perturbation methods of refs. 7,8. In our calculations, the energy cut-off for plane waves was 550 eV, the spacing of k-points was less than 0.1 \AA^{-1} and the convergence condition was that the total energy difference be less than $1 \mu\text{eV}$. The relaxed structural parame-

*E-mail: fukuda@spring8.or.jp

†E-mail: baron@spring8.or.jp

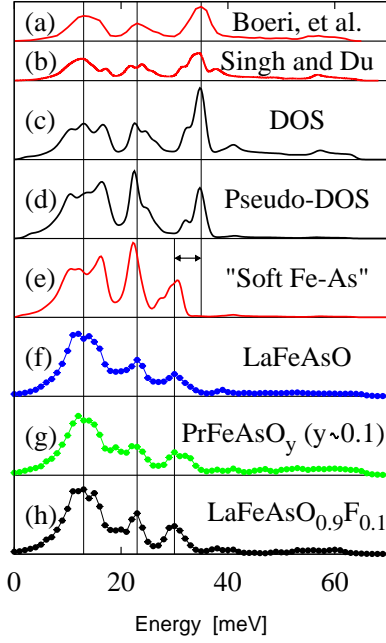


Fig. 1. Calculated and measured densities of states. The usual phonon density of states from (a) Boeri *et al.*,⁸ (b) Singh *et al.*,⁷ and (c) this work. (d) The pseudo-DOS and (e) the effect of softening only the Fe-As bond (see discussion in text). (f)-(h) The pseudo-DOS extracted from measurements of three samples (see the Appendix for details on data processing). Vertical lines are at 13, 23, 30 and 35 meV, while the horizontal arrow shows the 5 meV shift between the room temperature measurements and the nominal calculation. The improved agreement with the soft Fe-As model is clear.

ters were found to be $a=4.0219$ Å and $c=8.6215$ Å with $z_{La}=0.14496$ and $z_{As}=0.63817$, similar to refs. 7, 8.

Figure 1 shows both the results of our calculations, and the data from several samples. The upper panels show the agreement of our calculated phonon DOS with previous work, and also the evolution of the DOS to the “pseudo-DOS” to be compared with experiment. By pseudo-DOS we mean the calculated one-phonon x-ray scattering integrated over the experimental range of momentum transfers. In this case, we use a momentum full width of 3.7 nm⁻¹ (corresponding to the acceptance of the analyzer array) centered at a momentum transfer of about 82 nm⁻¹ – the precise value (fluctuation < 1 nm⁻¹) was sample dependent and was chosen to reduce the elastic contribution due to Bragg peaks. The DOS to pseudo-DOS transformation leaves the fine structure nearly unaffected, while changing the over-all weighting of the peaks. What is crucial for our discussion is that the triplet peak structure, with a broad peak at 13 meV and narrower ones at 23 and 35 meV remains robust, independent of which quantity is plotted.

The lower half of Fig. 1 compares the extracted pseudo-DOS (see the appendix for details on data treatment) to the calculation. For all compounds, the first and second peaks agree reasonably with the calculation for LaFeAsO, however, the measured third peak is strongly softened, about 5 meV or 15%. Looking more closely, one also notes that the first peak is narrower experimen-

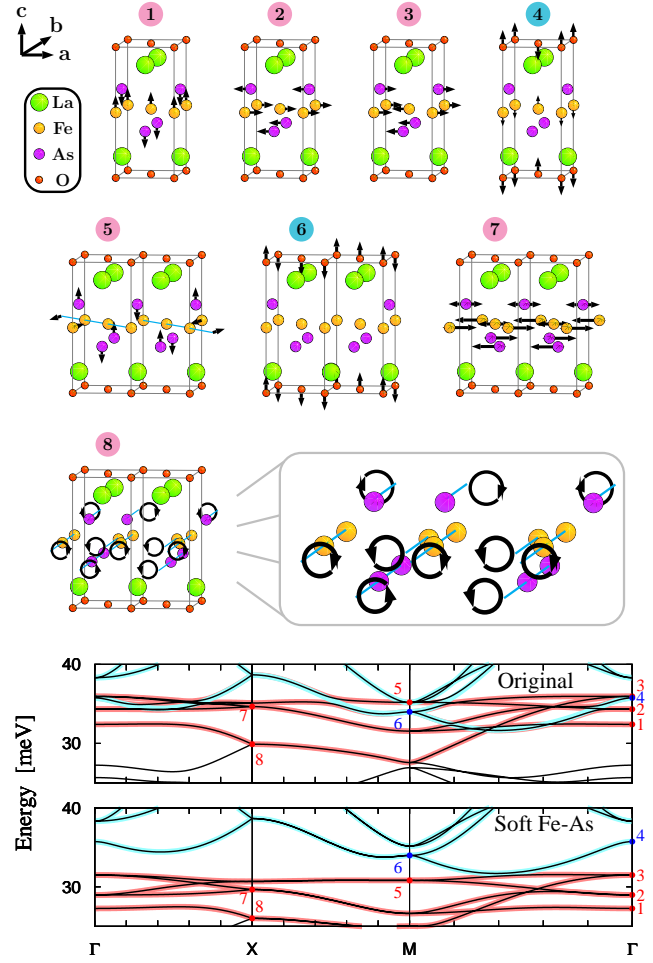


Fig. 2. Selected mode polarizations and dispersion. Polarizations are shown for the points indicated on the dispersion plots, with modes at M and X shown with two unit cells to allow the full phasing to be visualized. Modes at Γ are generally either planar or c -axis polarized, while modes at M and X can be mixed. Modes at X, in particular, are complex and can involve circular motions. Red (blue) shading indicates Fe-As (oxygen) modes. The effect of the soft Fe-As bond is primarily to shift the Fe-As modes to lower energy, as compared to the original calculations.

tally than calculated, while the second and third peaks are blurred out, and generally weaker than the calculated ones. We also note the presence of a weak peak at about 39 meV in some of the measured spectra, and also seen, at slightly higher energy, in the calculation. Overall, the clearest result is that the third peak in the DOS is softened. Considering the loss of definition of the peaks, however, one can speculate that the phonon modes between 10 and 35 meV are somewhat blurred out and soft, either due to band broadening (increased dispersion), or, perhaps, lifetime effects. Our measured DOS results are consistent with ref. 14 (for $E < 20$ meV) and unpublished work.^{15,16}

The dispersion and the contribution to the phonon modes near 35 meV calculated peak appears somewhat complex (see Fig. 2 and also discussion in ref. 8). The relevant band of modes consists primarily of in-plane FeAs motion at Γ , but the dispersion of these modes through the zone is complicated by (1) mixing with the c -axis

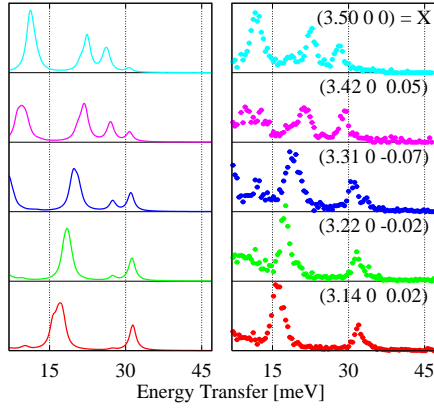


Fig. 3. Comparison of the measured dispersion for PrFeAsO_{1-y} ($y \sim 0.1$), $T_c = 36\text{ K}$ at room temperature (right panel) and calculation (left). See text for discussion.

polarized motion of the FeAs layers, and (2) the crossing of fast-dispersing oxygen modes. However, the peak in the pseudo-DOS is due nearly entirely to Fe-As motion. This can be demonstrated by softening *only* the Fe-As force constant matrix in the calculations. The resulting “soft Fe-As” pseudo-DOS calculation then agrees reasonably well with the data: a reduction of the Fe-As nearest neighbor force constant matrix to 70% of the calculated value brings the calculated peak into line with the measured one, and has only small effect on the rest of the spectrum.

This model is in reasonable agreement with measurements of a small, $150 \times 100 \times 20 \mu\text{m}^3$, single crystal of PrFeAsO_{1-y} ($y \sim 0.1$), $T_c = 36\text{ K}$. Figure 3 shows the dispersion along Γ -X in the (300) Brillouin zone. The high energy region shows the softening of the LO modes, essentially as expected from our model, excepting near the transfer ($H = 3.31, 3.42$) of intensity from mode 3 in Fig. 2 (an in-plane polarized LO mode) to mode 8 (a circular mode in the a - c plane), where the data shows a more abrupt transfer than the calculation. The transition point is sensitive to small changes in polarization, and could be affected by the oxygen nonstoichiometry. The slightly complex structures at lower energy come from exciting multiple nearby modes and are, partly, due to our finite momentum resolution [$\Delta Q = (0.067, 0.068, 0.035) \text{ rlu}$]. However, interestingly, the broad structure at about 10 meV at $(3.42, 0, 0.05)$ is actually in better agreement with the original calculations (not shown) and, will be the subject of future investigation. The remaining small discrepancies in the lower-energy modes, given the changes in system ($\text{La} \rightarrow \text{Pr}$), are not unreasonable. We note that available Raman data^{17,18} are in better agreement with the soft Fe-As model than the original calculation: the average energy difference between measurements and our calculation is reduced from 1.9 to 0.9 meV (for three modes)¹⁷ and from 2.0 to 0.9 meV (for five modes)¹⁸ when the softening is included in the model.

The softening of the phonons relative to the calculations suggests that there is some character of the interaction that is not properly included in the calculations, and

this interaction screens the phonons and reduces their energy. This is consistent with the tendency the LDA calculations to under-estimate the Fe-As bond distance (ie: 2.337 Å in the present calculation as compared to 2.407 Å measured in ref. 19). In this context we note that another large discrepancy between the calculations and measured data regards the determination of the magnetic moment on the iron atoms: the pseudopotential calculations²⁰ give consistently much larger iron moments (1 to 2 μ_B) than measurements (~ 0.2 - $0.4 \mu_B$).^{19,21,22} This has been, improved by going to an all-electron calculation,²³ but bond-lengths were not reported. Also, a negative U ²⁴ has been considered to account for this, but appears not to strongly affect the phonon energies. One pertinent fact, at least for the phonon question, regards the phase transition in the parent material LaFeAsO : it transforms from a tetragonal high temperature phase to an orthorhombic low temperature phase at about 145 K, with magnetic order setting at $\sim 140\text{ K}$ (see, e.g., refs. 19 and 21). Carefully relaxed calculations suggest that the energy barrier between the two possible orthorhombic configurations at low-temperature is very small ($\sim 5 \text{ meV}$),²⁵ well within phonon energy scales. Thus it is possible that anharmonicity plays a significant role in determining material properties. To investigate the effects of possible anharmonicity, we cooled the $\text{LaFeAsO}_{0.9}\text{F}_{0.1}$ powder sample to 35 K. We found the low-energy peak at 13 meV hardened slightly, $< 1 \text{ meV}$, the peak at 23 meV hardened about 1 meV, and the peak at 30 meV hardened about 1.5 meV, similar to refs. 15, 16. In order to get good agreement with calculation for the high-energy peak, we still have to soften the Fe-As force constant matrix by about 20%. While this does not rule out an anharmonic potential leading to softening of the Fe-As bond, it does clearly indicate that the strong softening we observe is predominantly intrinsic, not related to the room-temperature measurement.

In summary, our data shows that one peak in the phonon DOS at room temperature is softened by about 15% compared to LDA based calculations of LaFeAsO , and that this softening can be well modeled by reducing just the Fe-As nearest-neighbor force constant matrix by about 30% from the calculated value. This model is consistent with single crystal measurements. The softening of the peak in the pseudo-DOS is reduced to about 10% at 35 K, consistent with about 20% reduction in the Fe-As force constant, but is still large. We also see a general blurring out of the spectral peaks that could be consistent either with increased dispersion of the modes (band-broadening) or possibly lifetime broadening, though the latter is not likely based on the single crystal work. These suggest rather strongly that the phonon system of this material is not yet understood and that *perhaps* one should not yet discard a possible phonon mediated mechanism on the basis of the presently available calculations. If one were to assume the only effect of the softening on the Eliashberg function, α^2F , is to reduce some of the mode frequencies, then indeed it would make negligible change to the calculated T_c ,^{8,15} however, the source of the softening is not clear, and, if it is due to coupling to the electronic system (so changing the mode

dependent electron-phonon coupling) then the effect on calculated T_c could be larger. Notably, all samples investigated, including the non-superconducting parent compound, show similar phonon DOS, suggesting that some other change in, e.g., the electronic structure, switches on superconductivity with doping.

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Appendix: Data Analysis

The extraction of the “pseudo-DOS” from the measured scattering proceeds much has been done previously in neutron scattering. The procedure is exact in the case of pure incoherent scattering from a monoatomic harmonic solid at a well-defined momentum transfer, but approximate if there are significant other scattering processes, such as, in the present case, coherent scattering. A large range of integration over momentum space was chosen to attempt to maximize the effective incoherent contribution and an iterative fitting process was used to remove multiphonon contributions. This provides an approximation to the generalized DOS (GDOS) which we call the pseudo-DOS in the paper. Early work along these lines can be found in ref. 26 while a recent application to inelastic x-ray scattering, essentially based on the analysis for nuclear resonant scattering, is discussed in ref. 27. This treatment preserves most of the main features of the spectra, while scaling them more nearly in agreement with the true one-phonon scattering (see Fig. A-1). One should note that the extracted spectra at low energies are sensitive to the subtraction of the elastic peak, so that results below 8 meV should be taken as approximate.

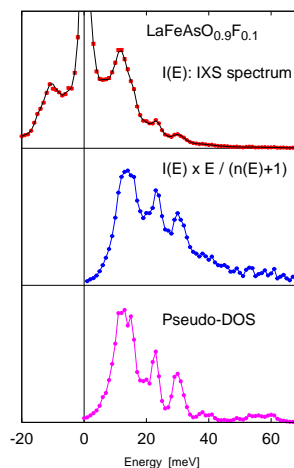


Fig. A-1. Analysis progression for one data set at 300K. The top panel shows the measured data. The middle panel shows a scaled version, after subtraction of the elastic peak, that would approximate the GDOS in the limit of pure incoherent single-phonon scattering. The lowest panel shows the extracted pseudo-DOS after the multi-phonon contributions were removed by an iterative procedure. Note the solid line in the top panel is the back-calculated scattering from the pseudo-DOS, and its good agreement with the measurement demonstrates the self-consistency of the procedure.

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